

# Desorption behavior of ammonia from TiO<sub>2</sub>-based specimens — ammonia sensing mechanism of double-layer sensors with TiO<sub>2</sub>-based catalyst layers

Yasuhiro Shimizu<sup>a,\*</sup>, Takayuki Okamoto<sup>a</sup>, Yuji Takao<sup>b</sup>, Makoto Egashira<sup>a</sup>

<sup>a</sup> Faculty of Engineering, Department of Materials Science and Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

<sup>b</sup> Faculty of Environmental Studies, Department of Environmental Studies, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

Received 5 October 1998; accepted 1 February 1999

## Abstract

Desorption behavior of gases from the NH<sub>3</sub>-preadsorbed catalyst and sensing materials used for double-layer semiconductor NH<sub>3</sub> sensors has been investigated under different adsorption and desorption conditions. The 0.5 Ir/TiO<sub>2</sub> catalyst material was found to exhibit mild activity for NH<sub>3</sub> oxidation and high activity for reducing NO to N<sub>2</sub> in an atmosphere containing NH<sub>3</sub> and O<sub>2</sub>. This nature was considered to be effective for reducing the interference from NO<sub>x</sub> at the vicinity of the interface between the catalyst layer and the In<sub>2</sub>O<sub>3</sub> sensing layer doped with 5 mol% MgO. The reduction of the interference led to high NH<sub>3</sub> sensitivity and a normal response to give a resistance decrease upon exposure to NH<sub>3</sub> even at higher temperatures. The abnormal response of a double-layer sensor with a 0.5 Pt/TiO<sub>2</sub> catalyst layer to give a resistance increase upon exposure to NH<sub>3</sub> especially at higher temperatures was confirmed to arise from its high NH<sub>3</sub> oxidation activity and low NO reduction activity. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Adsorption; Desorption; Double-layer sensor; Ammonia-gas sensing

## 1. Introduction

Ammonia-gas sensing has become increasingly important in controlling systems for various industrial processes and human comfort. Numerous efforts have been directed to developing highly sensitive NH<sub>3</sub> sensors by employing organic membranes, solid electrolytes and semiconductive metal oxides. Among them, most of the semiconductor gas sensors [1–5]

reported so far exhibit very small changes in resistance (or conductance) upon exposure to NH<sub>3</sub>, i.e., very low NH<sub>3</sub> sensitivity, except for an Au-loaded WO<sub>3</sub> sensor [6,7]. Interference from NO<sub>x</sub>, especially NO<sub>2</sub>, which is an oxidation product of NH<sub>3</sub> and is known to behave as an oxidizing gas [8,9], is presumed to be one of reasons for the low NH<sub>3</sub> sensitivity observed.

Actually, our previous study has shown that the interference from NO<sub>x</sub> is serious in detecting NH<sub>3</sub> by semiconductor gas sensors [10]. A single-layer n-type In<sub>2</sub>O<sub>3</sub> sensor doped with 5

\* Corresponding author.

mol% MgO {In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%)} and equipped with a pair of electrodes in its innermost region (Fig. 1a and b) exhibited a resistance decrease, i.e., a normal response, upon exposure to 300 ppm NH<sub>3</sub> at a temperature as low as 300°C. However, an abnormal response was observed above 500°C, an abrupt decrease in resistance, followed by a gradual increase to a higher level than that in air, upon exposure to NH<sub>3</sub>. Furthermore, an additional increase and a subsequent decrease in resistance were observed after removal of NH<sub>3</sub>. Such an abnormal response was further highlighted when the In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%) sensor was covered with a TiO<sub>2</sub> loaded with 0.5 wt.% Pt (0.5 Pt/TiO<sub>2</sub>) catalyst layer (Fig. 1c). The resistance of this

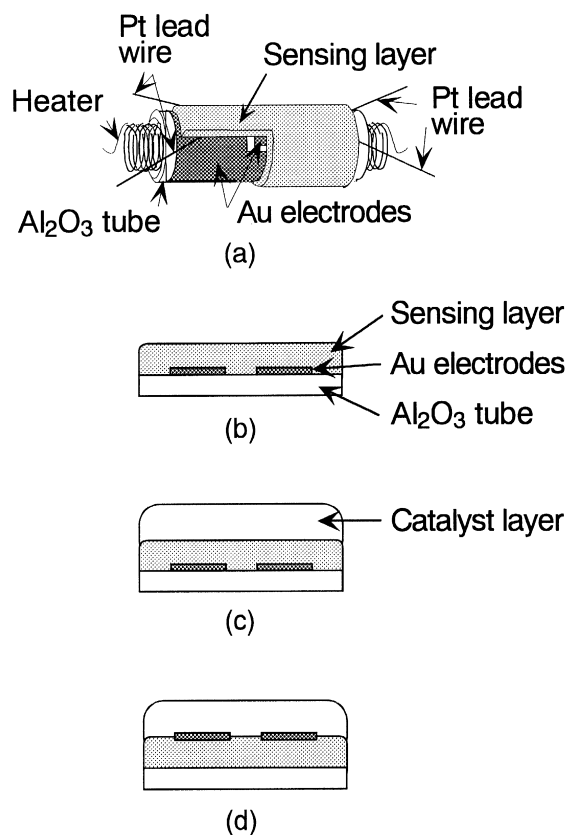


Fig. 1. Sensor structure. (a) An overview of a single-layer sensor (interior electrodes), (b) a cross section of a single-layer sensor (interior electrodes), (c) a double-layer sensor (interior electrodes) and (d) a double-layer sensor (interface electrodes).

double-layer sensor remained almost constant upon exposure to NH<sub>3</sub> at 370°C, but increased after removal of NH<sub>3</sub>. At 620°C, the resistance increased abruptly upon exposure to NH<sub>3</sub>, and further increased even after removal of NH<sub>3</sub>. Such abnormal response behavior is undoubtedly due to interference from NO<sub>x</sub>.

In contrast, we found that a double-layer sensor fabricated by coating an In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%) sensing layer with a 0.5 Ir/TiO<sub>2</sub> catalyst layer kept its normal response up to 620°C with relatively high NH<sub>3</sub> sensitivity, although the resistance level just after removal of NH<sub>3</sub> was slightly higher than the original air level. Furthermore, we succeeded to realize much higher NH<sub>3</sub> sensitivity and complete recovery to the original resistance level after removal of NH<sub>3</sub> even at 620°C by changing the electrode position from the innermost region of the sensing layer to the interface between the catalyst layer and the sensing layer (Fig. 1d). These results suggest that the control of oxidation behavior of NH<sub>3</sub> over the catalyst and sensing materials is important in developing highly sensitive NH<sub>3</sub> sensors.

In order to discuss the NH<sub>3</sub> sensing mechanism of the double-layer sensors and then to establish the guidelines on the design of semiconductor NH<sub>3</sub> sensors, the surface chemistry of NH<sub>3</sub> over the catalyst and sensing materials has been investigated by temperature programmed desorption technique (TPD) in the present study.

## 2. Experimental

### 2.1. Preparation of specimens

Titanium oxide was prepared by calcining the hydrolysis product of titanium tetrachloride at 1000°C for 1 h in air. The oxide was suspended in an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O, PdCl<sub>2</sub>, or IrCl<sub>3</sub> · H<sub>2</sub>O, followed by evaporation to dryness [11,12]. The amount of the metal

loaded was fixed at 0.5 wt.% in every case. The resultant solid was ground, and was subjected to reduction in flowing  $H_2$  at  $400^\circ C$  for 5 h.

$In_2O_3$ –MgO (5 mol%) as a sensing material was prepared in a dry process by mixing and grinding the constituent oxides, then calcining at  $1100^\circ C$  for 1 h in air. This process was repeated five times to ensure the solid solution of MgO into the  $In_2O_3$  lattice [13].

## 2.2. TPD measurement

TPD spectra of gaseous species from the  $NH_3$ -preadsorbed catalyst and sensing specimens were measured in a conventional flow apparatus under different adsorption and desorption conditions. The powder of the specimens was pressed into disks and then crushed to granules (40–60 mesh). The granules of each specimen (3.0 g) was set in the apparatus, and then were preheated at  $700^\circ C$  for 1 h under a flowing gas mixture of 20%  $O_2$  and 80% He at a rate of  $30\text{ cm}^3\text{ min}^{-1}$ . In a cooling procedure the flowing gas was switched to another flowing gas, as indicated below, at  $130^\circ C$ . At the same temperature and in the same flowing gas, the granules were kept for 30 min for adsorption. Then the granules were cooled to room tempera-

ture in the same flowing gas. To remove physically adsorbed water, which may be produced by the oxidation of  $NH_3$  with oxygen adsorbates during the adsorption procedure, the granules were again heated at  $120^\circ C$  for 30 min under flowing pure He at a rate of  $10\text{ cm}^3\text{ min}^{-1}$ . The granules were again cooled to room temperature under the same flowing. Thereafter, the TPD spectra were measured up to  $700^\circ C$  at a heating rate of  $5^\circ C\text{ min}^{-1}$  in different flowing gases. The adsorption and desorption conditions were as follows:

1. Ads: 500 ppm  $NH_3$ –0.2%  $O_2$ –99.75% He;  
Des: 100% He
2. Ads: 500 ppm  $NH_3$ –0.2%  $O_2$ –99.75% He;  
Des: 300 ppm  $NH_3$ –20%  $O_2$ –79.97% He
3. Ads: 500 ppm NO–0.2%  $O_2$ –99.75% He;  
Des: 100% He

The No. 3 condition was conducted to confirm the surface reaction of NO with oxygen adsorbates over the specimens. The desorbed gases were analyzed by gas chromatography mass spectrometry (GC-MS, QP-5000, Shimadzu) every 3 min. The detection limits of  $NH_3$  and NO by GC-MS were about 400 and 200 ppm, re-

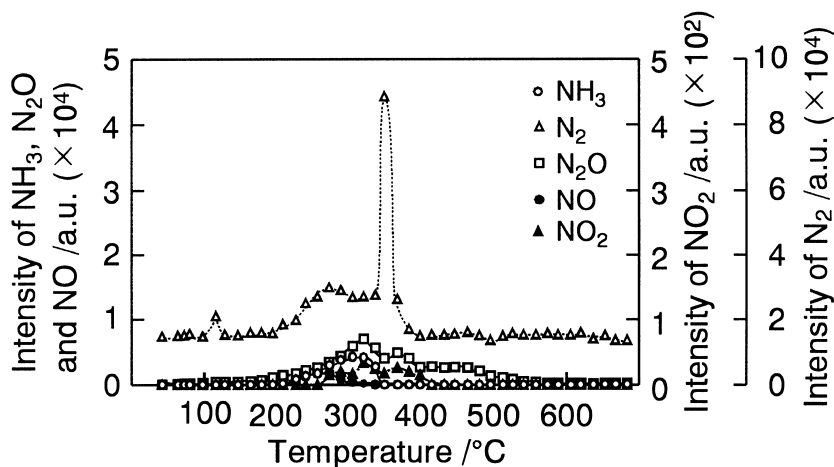


Fig. 2. Desorption behavior of gases from  $NH_3$ -preadsorbed 0.5 Ir/ $TiO_2$  (ads: 500 ppm  $NH_3$ –0.2%  $O_2$ –99.75% He, des: 100% He).

spectively. However, GC-MS detection of a low  $\text{NO}_2$  concentration was difficult in the present study. Thus, the TPD peaks observed for these species correspond to concentrations higher than the limits.

### 3. Results

#### 3.1. Desorption behavior of $\text{NH}_3$ under flowing pure He

Fig. 2 shows TPD spectra of gases desorbed from the  $\text{NH}_3$ -preadsorbed 0.5 Ir/ $\text{TiO}_2$  measured under condition No. 1. The vertical axes represent the GC-MS intensities of the desorbed gases. Thus, the intensity does not directly mean the amount of a gas desorbed, but corresponds to a relative desorption rate of the gas. In addition, the intensity is plotted in an arbitrary unit, since quantitative analysis was not carried out for every gas in the present study. Therefore, the magnitude of the intensity cannot be compared among different gases, but can be a measure of the desorption rate for the same gas.

Under experimental condition No. 1, maximum desorption peaks of NO,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{N}_2$  were observed around 273°, 305°, 320°, 320°, and 349°C, respectively. Although some amounts of NO,  $\text{N}_2\text{O}$  and  $\text{NO}_2$  had already been produced during the  $\text{NH}_3$ -preadsorption procedure, some amounts of these species may be produced by the reaction of the adsorbed  $\text{NH}_3$  with oxygen adsorbates during the desorption run to give some contribution to the TPD peaks. On the other hand,  $\text{N}_2$  is suggested to be produced by the reduction of NO with  $\text{NH}_3$  during the desorption run [14,15]. Thus, the  $\text{N}_2$  intensity can be regarded as a measure of the ability for reducing the interference from NO when the specimen is used as a catalyst layer in the double-layer  $\text{NH}_3$  sensors.

Desorption behavior of each gas is compared among the specimens in Fig. 3. For easy comparison of the data, the maximum scale of the

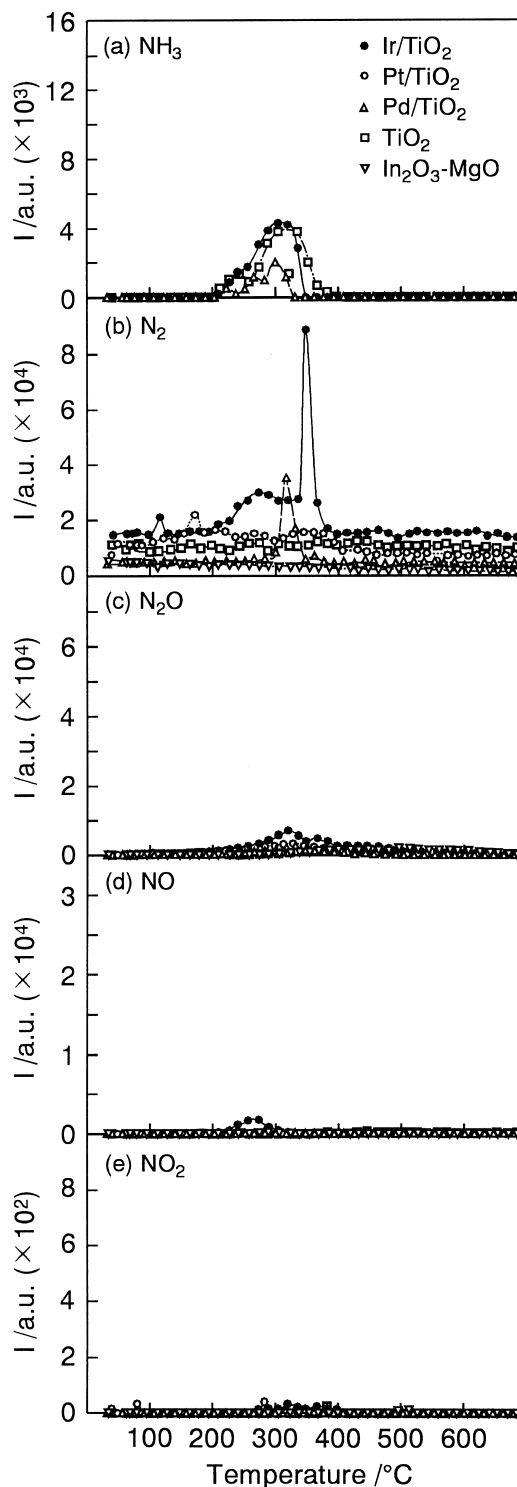


Fig. 3. Desorption behavior of gases from the  $\text{NH}_3$ -preadsorbed catalyst and sensing materials (ads: 500 ppm  $\text{NH}_3$ -0.2%  $\text{O}_2$ -99.75% He, des: 100% He).

vertical axis is kept constant for each gas throughout the present paper. The desorption of  $\text{NH}_3$  was observed with  $\text{TiO}_2$  and  $0.5 \text{ Pd}/\text{TiO}_2$  around  $300^\circ\text{C}$  as shown in Fig. 3a, but it was negligible in the cases of  $0.5 \text{ Pt}/\text{TiO}_2$  and  $\text{In}_2\text{O}_3\text{-MgO}$  (5 mol%). Among the specimens tested,  $0.5 \text{ Ir}/\text{TiO}_2$  exhibited the highest  $\text{N}_2$  desorption peak (Fig. 3b). Compared with the results obtained under different conditions shown in the below, the desorption peaks of  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  were small for every specimen under flowing pure He (Fig. 3c–e).

### 3.2. Desorption behavior of $\text{NH}_3$ under a flowing gas mixture of $\text{NH}_3$ , $\text{O}_2$ and He

To get information on the desorption behavior of  $\text{NH}_3$  in the atmosphere of  $\text{NH}_3$  sensitivity measurement, TPD spectra were measured under a flowing gas mixture of 300 ppm  $\text{NH}_3$ , 20%  $\text{O}_2$  and 79.97% He. The  $\text{NH}_3$  desorption peaks in Fig. 4a were obviously enlarged in comparison with those in Fig. 3a, except for that from  $0.5 \text{ Pt}/\text{TiO}_2$ . Again, no  $\text{NH}_3$  desorption was observed from  $0.5 \text{ Pt}/\text{TiO}_2$ . Additional adsorption of  $\text{NH}_3$  during the desorption run up to around  $100^\circ\text{C}$  is anticipated to be responsible for the enlargement. Besides  $0.5 \text{ Ir}/\text{TiO}_2$ , only  $0.5 \text{ Pt}/\text{TiO}_2$  showed a clear  $\text{N}_2$  desorption peak around  $163^\circ\text{C}$ , but it was lower than that of  $0.5 \text{ Ir}/\text{TiO}_2$ , as shown in Fig. 4b. Thus, it is shown that  $0.5 \text{ Ir}/\text{TiO}_2$  exhibits the highest activity for reducing  $\text{NO}$  to  $\text{N}_2$  among the specimens tested including the sensing material. Desorption peaks of  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  were also increased for every specimen under condition no. 2, due to both the increased amounts of adsorbed  $\text{NH}_3$  and the reaction of gaseous  $\text{NH}_3$ , which was contained in the carrier gas, with oxygen adsorbates and/or gaseous  $\text{O}_2$ . Especially,  $0.5 \text{ Pt}/\text{TiO}_2$  exhibited the maximum desorption peaks of  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  around  $163^\circ\text{C}$ , and their intensities were much larger than those observed with other specimens. These results imply the high catalytic activity of  $0.5 \text{ Pt}/\text{TiO}_2$

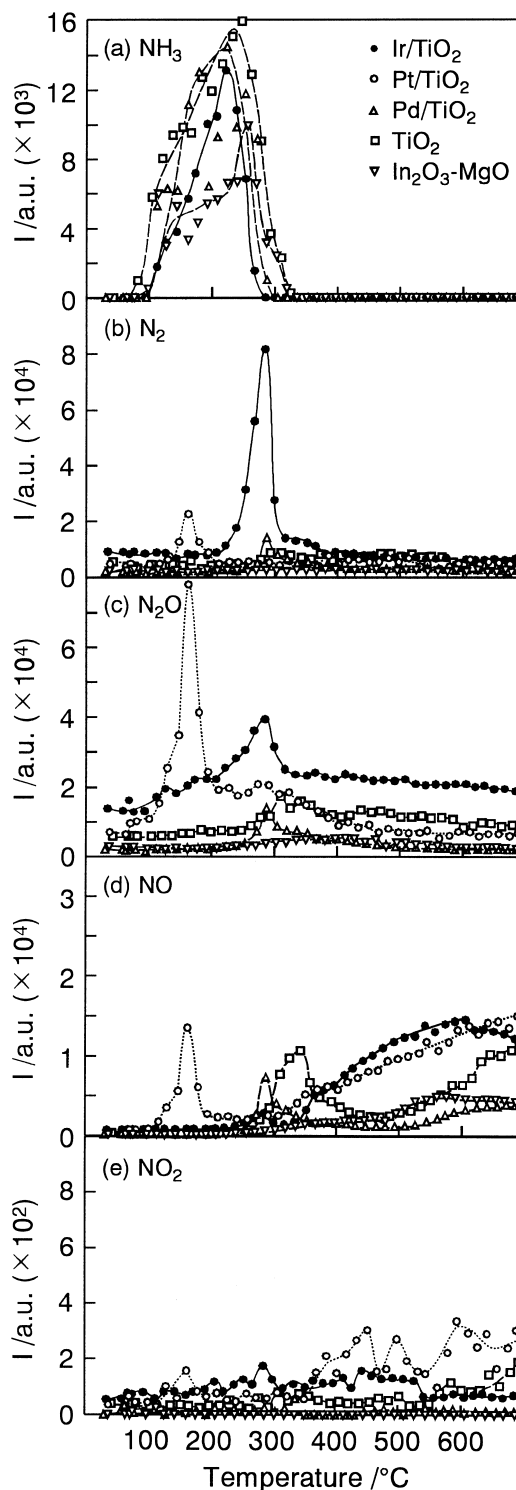


Fig. 4. Desorption behavior of gases from the  $\text{NH}_3$ -preadsorbed catalyst and sensing materials (ads: 500 ppm  $\text{NH}_3$ -0.2%  $\text{O}_2$ -99.75% He, des: 300 ppm  $\text{NH}_3$ -20%  $\text{O}_2$ -79.97% He).

for the oxidation of  $\text{NH}_3$ . Relatively large desorption peaks of NO and  $\text{NO}_2$  observed with most specimens above  $400^\circ\text{C}$  are considered to arise mainly from the reaction of gaseous  $\text{NH}_3$  with oxygen adsorbates and/or gaseous  $\text{O}_2$ .

### 3.3. Desorption behavior of NO under flowing pure He

To get information on the oxidation behavior of NO over the specimens and also on the

desorption behavior of gases from NO-preadsorbed specimens, TPD spectra were measured under condition No. 3. A desorption peak of  $\text{N}_2\text{O}$  was clearly observed around  $274^\circ\text{C}$  only with  $0.5 \text{ Ir}/\text{TiO}_2$ , as shown in Fig. 5a. The specimen  $0.5 \text{ Ir}/\text{TiO}_2$  also exhibited a large desorption peak of NO around  $226^\circ\text{C}$ , but a small desorption peak of  $\text{NO}_2$ , as shown in Fig. 5b and c, respectively. In contrast,  $0.5 \text{ Pt}/\text{TiO}_2$  exhibited the highest desorption peaks of NO and  $\text{NO}_2$  among the specimens tested. Furthermore, it is obvious that the desorption peak of  $\text{NO}_2$  shifted from  $419^\circ\text{C}$  to  $306^\circ\text{C}$  by the addition of 0.5 wt.% Pt to  $\text{TiO}_2$ , as shown in Fig. 5c. These results confirm that the catalytic activity for the oxidation of NO is enhanced by the addition of Pt, and that  $0.5 \text{ Pt}/\text{TiO}_2$  exhibits the highest activity among the specimens tested.

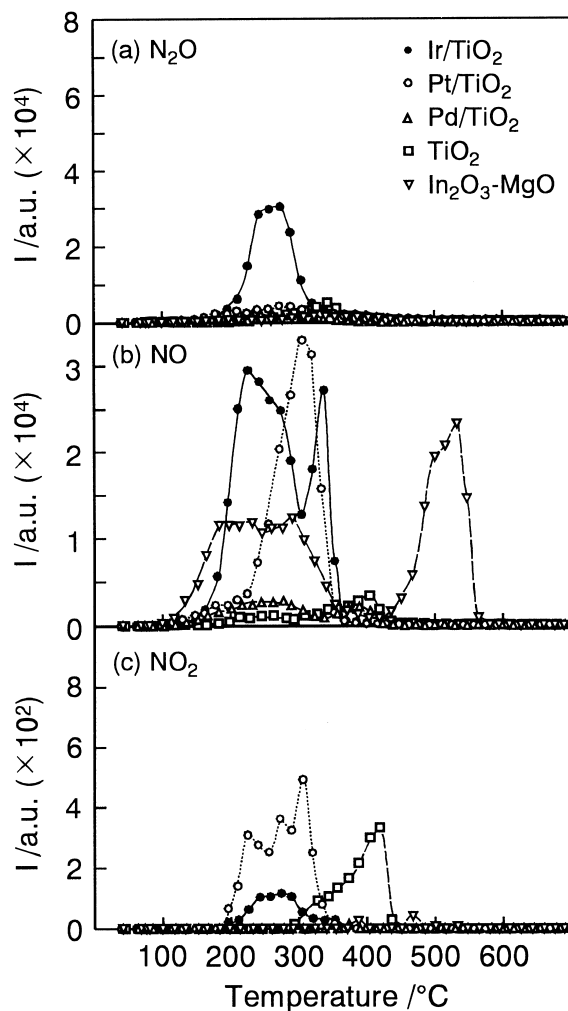


Fig. 5. Desorption behavior of gases from the NO-preadsorbed catalyst and sensing materials (ads: 500 ppm NO–0.2%  $\text{O}_2$ –99.75% He, des: 100% He).

## 4. Discussion

Table 1 summarizes the sensing properties to 300 ppm  $\text{NH}_3$  in air of double-layer sensors consisting of a catalyst layer, an  $\text{In}_2\text{O}_3$ – $\text{MgO}$  (5 mol%) sensing layer and interface electrodes, and the desorption data from the  $\text{NH}_3$ -preadsorbed catalyst and sensing materials under condition No. 2. The sensing properties were cited from our previous study [10]. Here, the sensitivity is defined as the ratio of sensor resistance in air to that in 300 ppm  $\text{NH}_3$ . For reference, the desorption behavior of gases from  $\text{NH}_3$ -preadsorbed  $\text{TiO}_2$  is also listed in Table 1.

The maximum sensitivity to 300 ppm  $\text{NH}_3$  of a thick film  $\text{In}_2\text{O}_3$ – $\text{MgO}$  (5 mol%) sensor equipped with a pair of electrodes on the sensor surface was 1.3 at most, and was observed at  $300^\circ\text{C}$ . The coating of this sensor surface with a catalyst layer, i.e., fabrication of a double-layer sensor with interface electrodes, resulted in an increase in  $\text{NH}_3$  sensitivity. However, the magnitude of the sensitivity enhancement was markedly dependent on the kind of the catalyst

Table 1

The sensing properties to 300 ppm NH<sub>3</sub> of double-layer sensors consisting of a catalyst layer, an In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%) sensing layer and interface electrodes, and the desorption data of gases from the NH<sub>3</sub>-preadsorbed catalyst and sensing materials

Catalyst layer	NH <sub>3</sub> sensing properties		Intensity (a.u.) and temperature (°C) of desorption <sup>a</sup>									
	$k_M^b$	$T_M^c$ (°C)	NH <sub>3</sub>		N <sub>2</sub>		N <sub>2</sub> O		NO		NO <sub>2</sub>	
			$I$	$T$	$I$	$T$	$I$	$T$	$I$	$T$	$I$	$T$
none <sup>d</sup>	1.3	300	$1.0 \times 10^4$	257	$2.8 \times 10^3$	462	$5.2 \times 10^3$	413	$4.9 \times 10^3$	560	$2.6 \times 10$	115
0.5 Ir/TiO <sub>2</sub>	64–97	470	$1.2 \times 10^4$	222	$8.0 \times 10^4$	285	$4.0 \times 10^4$	285	$1.5 \times 10^4$	605	$1.7 \times 10^2$	285
0.5 Pd/TiO <sub>2</sub>	16–23	530	$1.5 \times 10^4$	224	$1.4 \times 10^4$	288	$1.4 \times 10^4$	288	$7.3 \times 10^3$	288	$5.7 \times 10$	336
0.5 Pt/TiO <sub>2</sub>	3.0–12	340	no	–	$2.3 \times 10^4$	163	$7.9 \times 10^4$	163	$1.4 \times 10^4$	163	$3.3 \times 10^2$	593
TiO <sub>2</sub>	–	–	$1.6 \times 10^4$	248	$8.5 \times 10^3$	311	$1.8 \times 10^4$	311	$1.1 \times 10^4$	343	$1.9 \times 10^2$	692

<sup>a</sup>TPD spectra were measured under a flowing gas mixture of 300 ppm NH<sub>3</sub>, 20% O<sub>2</sub> and 79.97% He by employing materials subjected to NH<sub>3</sub> preadsorption under a flowing gas mixture of 500 ppm NH<sub>3</sub>, 0.2% O<sub>2</sub> and 99.75% He.

<sup>b</sup>Maximum sensitivity to 300 ppm NH<sub>3</sub>.

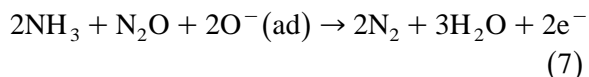
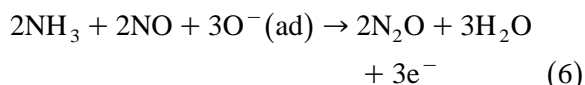
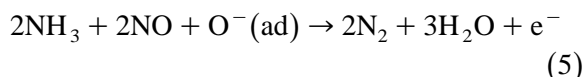
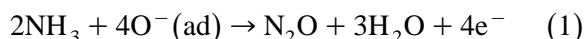
<sup>c</sup>Operating temperature for  $k_M$ .

<sup>d</sup>In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%) as a sensing material.

layer. The most significant improvement was achieved with 0.5 Ir/TiO<sub>2</sub> at 470°C. In addition, the resistance of the double-layer sensor with a 0.5 Ir/TiO<sub>2</sub> catalyst layer recovered to the original air level after removal of NH<sub>3</sub> over the whole temperature range of 340° to 620°C [10]. Although the coating with 0.5 Pt/TiO<sub>2</sub> led to a slight increase in sensitivity at 340°C, the resistance of the double-layer sensor after removal of NH<sub>3</sub> became higher than the original air level even at this temperature. This behavior became more significant at higher temperatures. Above 530°C the resistance in 300 ppm NH<sub>3</sub> was higher than the original air level, and a further increase in resistance was observed just after removal of NH<sub>3</sub>. In the case of the double-layer sensor with a 0.5 Pd/TiO<sub>2</sub> catalyst layer, such an abnormal response was not observed up to 620°C, whereas the sensitivity enhancement was less significant than that for the coating with 0.5 Ir/TiO<sub>2</sub>.

Based on the present desorption behavior of gases from the NH<sub>3</sub>-preadsorbed materials, the reaction of NH<sub>3</sub> in the double-layer sensors and their NH<sub>3</sub> sensing mechanism are discussed below. The following reactions are likely to

occur over the present catalyst and sensing materials.



Here, O<sup>−</sup>(ad) represents oxygen adsorbate, and reactions of NH<sub>3</sub> with gaseous O<sub>2</sub> are ruled out due to no direct electronic interaction with the sensing material.

In the case of the double-layer sensor with interface electrodes employed in our previous study, it is of no doubt that chemical reactions in the vicinity of the interface between the catalyst and the sensing layer primarily regulate the electrical properties of the sensing layer.

When 0.5 Ir/TiO<sub>2</sub> is employed as a catalyst layer, most of NH<sub>3</sub> is anticipated to diffuse into the interface through pores in the catalyst layer due to relatively low oxidation activity of the catalyst layer itself, as schematically shown in Fig. 6a. Then the resistance of the sensing material, n-type In<sub>2</sub>O<sub>3</sub>–MgO (5 mol%), decreases due to the reactions (1) and (2) at the interface. The N<sub>2</sub>O produced according to Eq. (1) is suggested to exhibit weak electronic interaction with the sensing material, and most of them go out of the sensor. In contrast, the NO produced according to Eq. (2) may directly affect the electronic properties of the sensing material by its chemisorption in the form of NO<sup>–</sup>(ad) or NO<sup>+</sup>(ad). Another possibility is that NO<sub>2</sub> produced by the oxidation of NO with gaseous oxygen may chemisorb on the sensing material and then increase the sensor resistance according to Eqs. (3) and (4). However, the 0.5 Ir/TiO<sub>2</sub> catalyst layer is considered to exhibit high activity for reducing NO to N<sub>2</sub> under the presence of NH<sub>3</sub> and O<sub>2</sub> according to Eq. (5) or

Eqs. (6) and (7). The progress of the reactions (2) and (5)–(7) results in a decrease in the sensor resistance, leading to high normal NH<sub>3</sub> sensitivity of the double-layer sensor with the 0.5 Ir/TiO<sub>2</sub> catalyst. Therefore, it is concluded that the high NH<sub>3</sub> sensitivity and the normal response arise mainly from the high activity of 0.5 Ir/TiO<sub>2</sub> for reducing NO to N<sub>2</sub>.

On the other hand, most of NH<sub>3</sub> is anticipated to be oxidized to N<sub>2</sub>O, NO and NO<sub>2</sub> during the diffusion through the 0.5 Pt/TiO<sub>2</sub> catalyst layer due to its high NH<sub>3</sub> oxidation activity, as schematically shown in Fig. 6b. This is supported by the fact that no NH<sub>3</sub> desorption peak is observed in the TPD spectrum, whereas large desorption peaks of N<sub>2</sub>O and NO are observed even at low temperatures, as summarized in Table 1. This is one of reasons for the lower NH<sub>3</sub> sensitivity of the double-layer sensor with the 0.5 Pt/TiO<sub>2</sub> catalyst layer than the sensor with the 0.5 Ir/TiO<sub>2</sub> catalyst, because the steady-state NH<sub>3</sub> concentration at the interface of the former becomes lower than that of the latter. Especially at temperatures higher than 350°C, the largest NO<sub>2</sub> desorption peak was observed with 0.5 Pt/TiO<sub>2</sub> among the specimens tested (Fig. 4e). Furthermore, 0.5 Pt/TiO<sub>2</sub> is less active than 0.5 Ir/TiO<sub>2</sub> for reducing NO to N<sub>2</sub>. Thus, the double-layer sensor with the 0.5 Pt/TiO<sub>2</sub> catalyst layer is likely interfered from NO<sub>x</sub>, leading to an abnormal response to NH<sub>3</sub> even at low temperatures. These results confirm that the abnormal response to NH<sub>3</sub> arises from both the high activity for NH<sub>3</sub> oxidation and the low activity for NO reduction of 0.5 Pt/TiO<sub>2</sub>.

Due to the mild NH<sub>3</sub> oxidation activity of 0.5 Pd/TiO<sub>2</sub>, in comparison with 0.5 Pt/TiO<sub>2</sub>, the double-layer sensor with the 0.5 Pd/TiO<sub>2</sub> catalyst layer is anticipated to exhibit the intermediate NH<sub>3</sub> sensing properties between the sensors with 0.5 Ir/TiO<sub>2</sub> and 0.5 Pt/TiO<sub>2</sub>. Based on the above results, it may be argued that a thicker catalyst layer enhances the interference from NO<sub>x</sub>, even if its catalytic activity for NH<sub>3</sub> oxidation is moderate.

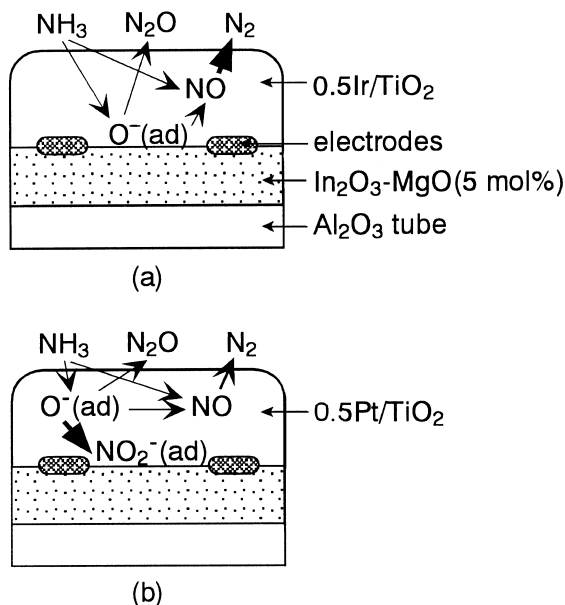


Fig. 6. Schematic drawing of the reactions of NH<sub>3</sub> in the double-layer sensors with (a) a 0.5 Ir/TiO<sub>2</sub> catalyst layer and (b) a 0.5 Pt/TiO<sub>2</sub> catalyst layer.



## 5. Conclusion

Comparison of the TPD spectra from the  $\text{NH}_3$ -preadsorbed catalyst and sensing materials under a flowing gas mixture of  $\text{NH}_3$ ,  $\text{O}_2$  and He has revealed that the 0.5 Ir/ $\text{TiO}_2$  catalyst material exhibited the highest  $\text{N}_2$  desorption peak and therefore the highest activity for reducing NO to  $\text{N}_2$ . In contrast, 0.5 Pt/ $\text{TiO}_2$  exhibited the largest desorption peaks of  $\text{N}_2\text{O}$ , NO and  $\text{NO}_2$  around  $163^\circ\text{C}$  and a further large  $\text{NO}_2$  desorption peak above  $370^\circ\text{C}$ , showing its high activity for  $\text{NH}_3$  oxidation and low activity for NO reduction. Therefore, it is concluded that the high  $\text{NH}_3$  sensitivity of a double-layer sensor with a 0.5 Ir/ $\text{TiO}_2$  catalyst layer to give normal decreases in resistance, which was reported in our previous study, arises mainly from its high activity for reducing NO to  $\text{N}_2$ , i.e., reducing interference from  $\text{NO}_x$  to the sensor response. It is also confirmed that the complex response to  $\text{NH}_3$  of a double-layer sensor with a 0.5 Pt/ $\text{TiO}_2$  catalyst layer to give decreases or increases in resistance arises from both the high activity for  $\text{NH}_3$  oxidation and the low activity for NO reduction.

To realize high  $\text{NH}_3$  sensitivity with semiconductor gas sensors, therefore, it is important to design the catalyst and sensing materials so as to exhibit moderate  $\text{NH}_3$  oxidation activity and high NO to  $\text{N}_2$  reduction activity. Further-

more, the sensor configuration such as electrode position and thickness of the catalyst and sensing layers is also important.

## References

- [1] P.J. Shaver, Appl. Phys. Lett. 11 (1967) 255.
- [2] H. Nanto, T. Minami, S. Takata, J. Appl. Phys. 60 (1986) 482.
- [3] G. Rosse, M. Ghers, J. Lebigot, J. Guyader, Y. Laurent, Y. Colin, Sens. Actuators 14 (1988) 133.
- [4] P.T. Moseley, D.E. Williams, Sens. Actuators, B 1 (1990) 113.
- [5] V.V. Malyshev, A.V. Eryshkin, E.A. Kolytyn, A.E. Varfolomeev, A.A. Vasiliev, Sens. Actuators, B 18–19 (1994) 434.
- [6] T. Maekawa, J. Tamaki, N. Miura, N. Yamazoe, Chem. Lett. 1992 (1992) 639.
- [7] M. Ando, T. Tsuchida, S. Suto, T. Suzuki, C. Nakayama, N. Miura, N. Yamazoe, J. Ceram. Soc. Jpn. 104 (1996) 1112.
- [8] M. Akiyama, J. Tamaki, N. Miura, N. Yamazoe, Chem. Lett. 1991 (1991) 1611.
- [9] G. Sberveglieri, L. Depero, S. Gropelli, P. Nelli, Sens. Actuators, B 26–27 (1995) 89.
- [10] Y. Takao, K. Miyazaki, Y. Shimizu, M. Egashira, J. Electrochem. Soc. 141 (1994) 1928.
- [11] Y. Takao, Y. Iwanaga, Y. Shimizu, M. Egashira, Sens. Actuators, B 10 (1993) 229.
- [12] Y. Shimizu, A. Kawasoe, Y. Takao, M. Egashira, in: H.U. Anderson, M. Liu, N. Yamazoe (Eds.), Ceram. Sens. III, Electrochem. Soc. Proc. 96–271996, p. 117.
- [13] Y. Takao, Y. Miya, Y. Tachiyama, Y. Shimizu, M. Egashira, Denki Kagaku 58 (1990) 1162.
- [14] E.T.C. Vogt, A. Boot, A.J. van Dillen, J.W. Geus, F.J.J.G. Janssen, F.M.G. van den Kerkhof, J. Catal. 114 (1988) 313.
- [15] R.B. Bjorklund, C.U.I. Odenbrand, J.G.M. Brandin, L.A.H. Andersson, B. Liedberg, J. Catal. 119 (1989) 187.